Kinetics of the Transformation of Halogenated Aliphatic Compounds by Iron Sulfide

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The transformation of nine halogenated aliphatic compounds by 10 g/L (0.5 m²/L) FeS at pH 8.3 was studied in batch experiments. These compounds were as follows: pentachloroethane (PCA), 1,1,2,2- and 1,1,1,2-tetrachloroethanes (1122-TeCA and 1112-TeCA), 1,1,1- and 1,1,2-trichloroethanes (111-TCA and 112-TCA), 1,1- and 1,2-dichloroethanes (11-DCA and 12-DCA), carbon tetrachloride (CT), and tribromomethane (TBM). 11-DCA, 12-DCA, and 112-TCA showed no appreciable transformation by FeS over approximately 120 days, but the other compounds were transformed with half-lives of hours to days. PCA and 1122-TeCA underwent dehydrohalogenation faster than FeS-mediated reductive dehalogenation reactions under the conditions of these experiments. The remaining compounds for which significant transformation was observed underwent FeS-mediated reactions more rapidly than hydrolysis or dehydrohalogenation. For 1112-TeCA, the dihaloelimination product (1,1-dichloroethylene) was the only reaction product detected. For 111-TCA, CT, and TBM, hydrogenolysis products were the only products detected, although their mass recoveries were considerably less than 100%. Two simple log-linear correlations between rate constants and either one-electron reduction potentials or homolytic bond dissociation enthalpies were developed, with coefficients of determination (R^2 values) of 0.48 and 0.82, respectively. These findings are consistent with a rate-limiting step involving homolytic bond dissociation. However, neither correlation accurately described the reactivity of all the compounds that were studied, suggesting distinctions among the mechanisms for reductive dehalogenation of these compounds by FeS or the influence of additional molecular or thermodynamic parameters on rate constants.

Introduction

Halogenated aliphatic compounds are common groundwater pollutants (*1, 2*) that are susceptible to reductive transformations in anaerobic environments. Many recent studies have focused on the abiotic transformation of these compounds by naturally occurring soil minerals such as iron sulfide (FeS) (*3–11*). Compounds reported to be transformed by FeS include hexachloroethane (HCA) (*9*), carbon tetrachloride (CT) (*4, 8, 10*), trichloroethylene (TCE) (*6, 7, 11*),

and tetrachloroethylene (PCE) (*11*). In related studies, the rates of transformation of HCA by biotite or vermiculite were observed to increase significantly when aqueous bisulfide was added to the experimental system (*12*), and transformation of CT by biotite or vermiculite plus aqueous bisulfide was also observed (*13*). The reactivity of the biotite/vermiculite bisulfide systems may have been due to the formation of a secondary iron sulfide phase upon reaction of bisulfide with ferrous iron associated with the clay minerals (*12, 13*). In contrast to the studies reporting reductive dehalogenation by FeS, other researchers have reported no transformation of CT (*3*), 1,1,1-trichloroethane (111-TCA) (*3*), TCE (*5*), or PCE (*3, 5*) in the presence of FeS. Differences in experimental conditions such as pH, dissolved oxygen concentration, and reaction time among the studies to date may be responsible for these sometimes inconsistent results.

The objectives of the experiments described here were 2-fold: first, to assess the relative rates and products of transformation of a variety of halogenated aliphatics by the soil mineral FeS under a uniform set of experimental conditions and, second, to establish whether there exists a relationship between rate constants for these transformations and free energy or molecular parameters. Such a relationship was sought to aid in understanding the influence of different molecular properties on reaction rates, to provide evidence about rate-limiting processes in these transformations, and to allow prediction of the rates of FeS-mediated reductive dehalogenation reactions in natural systems. Previous studies have correlated rate constants for reductive dehalogenation by anaerobic sediments (*14*), transition metal coenzymes (*15*), iron metal (*16–18*), mercaptojuglone (*19*), and iron porphyrins (*19*) with molecular properties such as reduction potential, bond dissociation energy, and lowest unoccupied molecular orbital (LUMO) energy.

Rates and products of the transformation of the following compounds by FeS are reported here: pentachloroethane (PCA), 1,1,2,2- and 1,1,1,2-tetrachloroethanes (1122-TeCA and 1112-TeCA), 111-TCA, 1,1,2-trichloroethane (112-TCA), 1,1- and 1,2-dichloroethanes (11-DCA and 12-DCA), CT, and tribromomethane (TBM). Previously reported results for the transformation of HCA (*9*), TCE (*11*), and PCE (*11*) by FeS are also discussed. These compounds were chosen for study based on their environmental relevance and also to obtain experimental data for a group of compounds possessing a range of the physical and chemical properties expected to influence reaction rates. Many are regulated under the United States Clean Water and Safe Drinking Water Acts and are common groundwater pollutants (*1, 2*).

Experimental Section

Materials and Procedures. Procedures for maintenance of anaerobic conditions and sterilization of aqueous solutions and glassware are described elsewhere (*9*). All chemicals were commercially available reagent or ACS grade and were used as received. Water was distilled and then purified using a Milli-Q Plus water system (Millipore Corp., Bedford, MA). FeS was prepared and characterized as described previously (*9*) as poorly crystalline mackinawite with a specific surface area of 0.05 m²/g. All samples contained 10 g/L (0.5 m²/L) FeS. The pH was buffered at 8.3 with 0.05 M each of tris-(hydroxymethyl)aminomethane (Tris) and Tris-HCl. Samples also contained 0.04 M NaCl and 0.01 N HCl, resulting in an ionic strength of 0.1 M.

Kinetic experiments were conducted in individual 5-mL flame-sealed glass ampules (*9*) to maintain anaerobic conditions and to prevent losses of volatile organic compounds

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during experiments of up to 4 months duration. After preparation, ampules were placed on Labindustries (Berkeley, CA) model T 415-110 rocking platform shaker at approximately 22 cycles/min in a temperature-controlled chamber at 25 °C in the dark. In each ampule, the aqueous phase volume was 5 mL, and the gas phase volume was approximately 2.82 mL. Transformation reactions were monitored over 3 or more half-lives, except for 11-DCA, 12-DCA, and 112-TCA, for which transformation reactions were monitored over the course of 120 days.

Samples were spiked with 50 μL of a 0.002 M solution of each halogenated aliphatic compound that had been prepared in N_2-sparged methanol, resulting in an aqueous solution containing 1% methanol by volume. Initial aqueous concentrations after partitioning to the sample headspace were determined by measurement of the aqueous concentration in the ionic medium alone (no FeS). Except for PCA and 1122-TeCA, aqueous concentrations measured in the ionic medium were used as the concentrations at time zero in fitting data to a pseudo-first-order rate law. For PCA and 1122-TeCA, for which dehydrohalogenation took place even in the absence of FeS, initial concentrations were those measured at the first sampling time in the presence of FeS, which was then considered to be time zero for these compounds.

Because methanol coeluted with vinyl chloride (VC), a potential reaction product, when using gas chromatography (GC) method B (described below), certain samples of 11-DCA, 12-DCA, and 112-TCA were also spiked with a 0.002 M solution prepared in 2-propanol. These samples were analyzed alongside samples spiked with methanol solutions for the purpose of determining whether VC was a reaction product for these compounds. Data from the 2-propanol-spiked samples were not used in rate constant determination.

At regular intervals during the course of the reaction, ampules were centrifuged at approximately 1000 rpm, broken open, and analyzed. PCA, 1122-TeCA, 1112-TeCA, 111-TCA, 112-TCA, CT, chloroform (CF), TBM, dibromomethane (DBM), PCE, TCE, and 1,1-dichloroethylene (11-DCE) were quantified by extraction of the aqueous supernatant into 2,2,4-trimethylpentane followed by analysis using GC method A (11). For PCA transformation experiments, the volume ratio of aqueous sample to extraction solvent was 75 μL/1.5 mL, and for all other experiments it was 100 μL/400 μL. For 112-TCA transformation experiments, the extraction solvent contained 3.2 μM TBM as an internal standard, and for PCA transformation experiments, it contained 6 μM 1,3,5-trichlorobenzene as an internal standard. For 1122-TeCA, 1112-TeCA, 111-TCA, CT, and TBM transformation experiments, no internal standard was used. Different internal standards (or no internal standard) were used in order to accurately determine concentrations for compounds with different GC retention times and for a range of GC operating conditions. Samples were analyzed in duplicate and quantified by comparison to a five-point standard curve. The results of duplicate analyses typically agreed within 1% using GC method A.

A 1-mL volume of the aqueous supernatant from certain samples was also analyzed for 11-DCA, 12-DCA, chloroethane, cis-1,2-dichloroethylene (cis-DCE), trans-1,2-dichloroethylene (trans-DCE), ethane, ethene, acetylene, dichloromethane, and methane using GC method B, which employed a Hewlett-Packard (Palo Alto, CA) 5890 GC with a HP 19395 headspace autosampler and an analytical method described elsewhere (9). Some samples were diluted in a 1:10 ratio prior to analysis. 11-DCA, 12-DCA, and 112-TCA samples spiked with a 2-propanol solution of the halogenated aliphatic compound were analyzed for VC using GC method B.

Samples from 11- and 12-DCA transformation experiments were analyzed using only GC method B. However, at least some samples from experiments with all other compounds, except PCA, were analyzed using both GC methods in order to identify as many reaction products as possible. Samples from PCA experiments were analyzed using only GC method A.

Treatment of Kinetic Data. Values of pseudo-first-order rate constants (k_{obs}) were determined by best fit of measured values of aqueous concentration as a function of time to a pseudo-first-order rate law. Values of k_{obs}', defined as the pseudo-first-order rate constant for disappearance of a compound in a hypothetical headspace-free system, were calculated using the procedure described in ref 11. Conversion of k_{obs} values to k_{obs}' values allowed valid comparison of rate constants for transformation of a series of compounds that have significantly different Henry's law constants. Mass recoveries were corrected as described in ref 11 to account for equilibrium partitioning of reactants and products between the aqueous and gas phases.

Dimensionless Henry's law constants (H values) used in these calculations were averages of all experimentally determined values at approximately 25 °C that were reported in refs 20–26, except that H_{CT} from ref 21 was eliminated as an outlier based on application of the Q test at the 95% confidence level. H_{PCA}, $H_{1112-TeCA}$, $H_{acetylene}$, and H_{DBM} were estimated, not experimentally measured, values reported in refs 27 (H_{PCA}, $H_{1112-TeCA}$, and $H_{acetylene}$) and 28 (H_{DBM}). These dimensionless Henry's law constants are as follows: HCA, 0.285; PCA, 0.0793; 1122-TeCA, 0.015; 1112-TeCA, 0.0989; 111-TCA, 0.622; 112-TCA, 0.0369; 11-DCA, 0.230; 12-DCA, 0.043; CT, 1.244; CF, 0.150; PCE, 0.764; TCE, 0.419; cis-DCE, 0.167; trans-DCE, 0.384; 11-DCE, 1.365; VC, 1.137; acetylene, 0.887; TBM, 0.023; and DBM, 0.04.

Results and Discussion

Reaction Pathways and Products. Table 1 summarizes the observed first-order rate constants, reaction products, mass recoveries, and reaction pathways for the transformation of 10 halogenated aliphatic compounds in the presence of FeS. Certain data for HCA in this table were reported previously (9). The rates of disappearance of 11-DCA, 12-DCA, and 112-TCA over 120 days were not sufficient to determine quantitative rate constants for disappearance of these compounds. Evidence for goodness of fit of the remaining data to a pseudo-first-order rate law includes the relatively small uncertainties associated with the rate constants reported in Table 1. In addition, the initial rate method (29, 30) was used previously (9) to show that transformation of HCA by 10 g/L FeS was first-order with respect to HCA (9) at concentrations similar to those used here.

Table 1 indicates that mass recoveries of reactants and products were considerably less than 100% in some cases. Low mass recoveries may be due to the formation of reaction products that would not have been detected using these analytical methods, inaccuracies in the Henry's law constants used in calculating mass recoveries, losses of volatile reactants and products during the sampling process, and adsorption of reactants and products to the FeS surface.

For each compound shown in Table 1, control experiments were concurrently performed using the ionic medium only and no FeS. Except for PCA, 1122-TeCA, and 112-TCA, there was no disappearance of any compound in the absence of FeS in the time scale of these experiments. PCA, 1122-TeCA, and 112-TCA underwent dehydrohalogenation (a nonreductive reaction) regardless of whether FeS was present. The rate constants, products, and mass recoveries for the dehydrohalogenation of PCA and 1122-TeCA in the ionic medium alone (no FeS) are reported in Table 2. Dehydrohalogenation of 1122-TeCA to TCE is also illustrated in Figure

TABLE 1. Observed First-Order Rate Constants, Products, Mass Recoveries, and Pathways for Transformation of Halogenated Aliphatic Compounds in the Presence of FeS

compound	k_{obs} (h^{-1})[a] $\{k_{obs}'$ (h^{-1})$\}$	products[b]	mass recovery (as %)[c]	pathway
HCA[d]	$(1.065 \pm 0.064) \times 10^{-1}$ $\{(1.236 \pm 0.074) \times 10^{-1}\}$	PCE PCA HCA remaining total	86 <1 <1 86	dihaloelimination hydrogenolysis
PCA	$(5.54 \pm 0.31) \times 10^{-1}$ $\{(5.79 \pm 0.32) \times 10^{-1}\}$	PCE TCE PCA remaining total	77 13 0 90	dehydrohalogenation dihaloelimination
1122-TeCA	$(1.298 \pm 0.087) \times 10^{-2}$ $\{(1.309 \pm 0.088) \times 10^{-2}\}$	TCE cis-DCE trans-DCE acetylene 1122-TeCA remaining total	58 3 <1 ~14 1 ~76	dehydrohalogenation see text dihaloelimination see text
1112-TeCA	$(3.05 \pm 0.51) \times 10^{-2}$ $\{(3.22 \pm 0.54) \times 10^{-2}\}$	11-DCE 1112-TeCA remaining total	62 <1 62	dihaloelimination
111-TCA	$(9.8 \pm 1.4) \times 10^{-3}$ $\{(1.32 \pm 0.19) \times 10^{-2}\}$	11-DCA 111-TCA remaining total	~2 4 ~6	hydrogenolysis
112-TCA	not known[e]	11-DCE VC 112-TCA remaining total	7 ~1 78 ~86	dehydrohalogenation dihaloelimination
11-DCA	not known[e]	11-DCA remaining[f]	99	no products detected
12-DCA	not known[e]	12-DCA remaining[f]	81	no products detected
CT	$(6.39 \pm 0.79) \times 10^{-2}$ $\{(1.09 \pm 0.13) \times 10^{-1}\}$	CF CT remaining total	46 0 46	hydrogenolysis
TBM	$(1.29 \pm 0.15) \times 10^{-1}$ $\{(1.31 \pm 0.15) \times 10^{-1}\}$	DBM TBM remaining total	3 0 3	hydrogenolysis

[a] Uncertainties are 95% confidence intervals. [b] For HCA, subsequent reaction products include TCE, cis-DCE, and acetylene (9). The PCA transformation experiment did not monitor for acetylene and DCEs. [c] Refer to text discussion for calculation of mass recoveries. [d] Data for HCA are from ref 9. [e] There was not sufficient transformation of this compound over the course of 120 days to determine a quantitative rate constant. [f] No reaction products were detected over the course of 120 days.

TABLE 2. Observed First-Order Rate Constants, Products, Mass Recoveries, and Pathways Transformation of Halogenated Aliphatic Compounds in the Ionic Medium Alone (no FeS)

compound	k_{obs} (h^{-1})[a] $\{k_{obs}'$ (h^{-1})$\}$	products[b]	mass recovery (as %)[c]	pathway
PCA	$(4.63 \pm 0.27) \times 10^{-1}$ $\{(4.84 \pm 0.28) \times 10^{-1}\}$	PCE PCA remaining total	92 0 92	dehydrohalogenation
1122-TeCA	$(1.11 \pm 0.39) \times 10^{-2}$ $\{(1.12 \pm 0.39) \times 10^{-2}\}$	TCE 1122-TeCA remaining total	90 9 99	dehydrohalogenation
112-TCA	not known[d]	11-DCE 112-TCA remaining total	7 83 91	dehydrohalogenation

[a] Uncertainties are 95% confidence intervals. See text for definitions of k_{obs} and k_{obs}'. [b] Only initial products are reported here. [c] Refer to text discussion for calculation of mass recoveries. [d] There was not sufficient transformation of this compound over the course of 120 days to determine a quantitative rate constant.

1a,b (open circles). Although the reaction of PCA and 1122-TeCA with FeS produced minor quantities of dihaloelimination products, rate constants for the disappearance of these compounds increased only slightly in the presence of FeS versus the ionic medium alone, as can be seen by comparison of Tables 1 and 2 and by inspection of Figure 1a, indicating that dehydrohalogenation by species present in the ionic medium, such as hydroxide ion, took place considerably faster than FeS-mediated reduction reactions for these compounds at pH 8.3 and 10 g/L FeS.

The mass recovery of the 112-TCA dehydrohalogenation product 11-DCE in the ionic medium alone is also reported in Table 2. Calculation of quantitative rate constants for the disappearance of 112-TCA in the presence or absence of FeS was not possible due to the slow rates of these reactions. In the presence of FeS, however, the mass recovery of the 112-
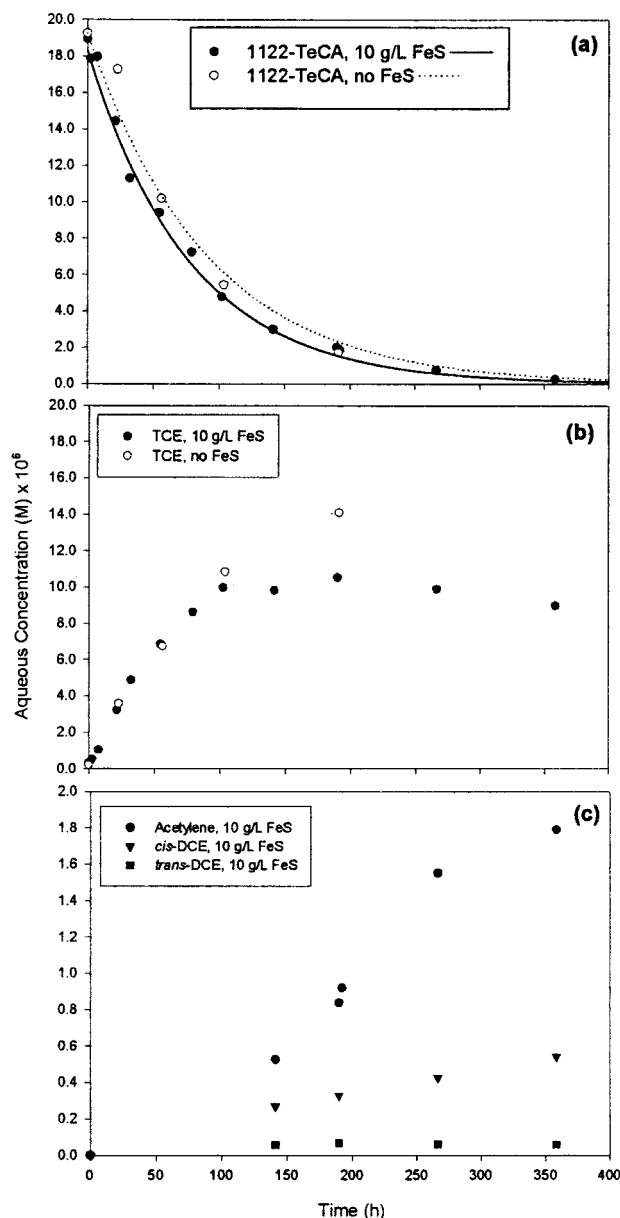
FIGURE 1. Aqueous concentrations of 1122-TeCA, TCE, acetylene, *cis*-DCE, and *trans*-DCE versus time; pH 8.3, 0.1 M Tris buffer, $I = 0.1$ M. The data points are experimentally measured values, the solid line is equal to $[1122 - TeCA]_{aq,0}e^{-k_{obs,FeS}t}$, where $k_{obs, FeS}$ equals $k_d + k_e$ and the dotted line is equal to $[1122 - TeCA]_{aq,0}e^{-k_d t}$ (see text). Aqueous concentrations of acetylene, *cis*-DCE, and *trans*-DCE were not measured at early time points. Acetylene, *cis*-DCE, and *trans*-DCE were detected only in samples containing FeS. Note that the *y*-axis scale for panel c differs from panels a and b.

TCA dehydrohalogenation product (11-DCE) was approximately 7% versus approximately 1% for its dihaloelimination product (VC) (Table 1). This indicates that, like PCA and 1122-TeCA, the rate of dehydrohalogenation of 112-TCA exceeds that of dihaloelimination under the conditions of these experiments. The more rapid dehydrohalogenation of PCA, 1122-TeCA, and 112-TCA as compared to the other halogenated organic compounds studied here is consistent with the results of Walraevens et al. (*31*) and Jeffers et al. (*32*), who found that the rates of dehydrohalogenation of a series of chlorinated ethanes in water followed the order PCA > 1122-TeCA > 112-TCA.

Rate constants for dihaloelimination of PCA and 1122-TeCA by FeS were estimated by subtracting the rate constant for PCA or 1122-TeCA disappearance in the absence of FeS

TABLE 3. Acetylene/*cis*-DCE Product Distribution Ratio as a Function of Time for 1122-TeCA Transformation by FeS[a]

time (h)	$\left[\dfrac{[\text{acetylene}]_{aq} \, f_{acetylene}}{[cis - \text{DCE}]_{aq} \, f_{cis-DCE}}\right]$[b]
141.2	2.7
189.8	3.5
266.4	5.0
358.3	4.5

[a] 10 g/L FeS, pH 8.3, 0.1 M Tris Buffer, $I = 0.1$ M. [b] This is the acetylene/*cis*-DCE product distribution ratio that would result in a hypothetical headspace-free system. The variable f_i is defined as $(1 + H_i V_g/V_{aq})$, where H_i is the dimensionless Henry's law constant of species i and V_g and V_{aq} are the gas- and aqueous-phase volumes, respectively, in each sample.

$[k_{obs, \text{no FeS}}$ (Table 2)] from the rate constant in the presence of FeS $[k_{obs, \text{FeS}}$ (Table 1)]. This assumes that $k_{obs, FeS}$ is equal to $k_d + k_e$, while $k_{obs, \text{no FeS}}$ is equal to k_d, where k_d is the pseudo-first-order rate constant for dehydrohalogenation and k_e is the pseudo-first-order rate constant for dihaloelimination. The resulting k_e values are $(9.1 \pm 4.1) \times 10^{-2}$ h^{-1} (PCA) and $(1.9 \pm 4.0) \times 10^{-3}$ h^{-1} (1122-TeCA). Plots of $[1122 - TeCA]_{aq,0}e^{-k_{obs,FeS}t}$ and $[1122 - TeCA]_{aq,0}e^{-k_d t}$ are shown along with experimentally measured aqueous concentrations in Figure 1a. The resulting k_e' values (corrected for partitioning between the aqueous and gas phases (*11*)) are $(9.5 \pm 4.3) \times 10^{-2}$ h^{-1} (PCA) and $(1.9 \pm 4.0) \times 10^{-3}$ h^{-1} (1122-TeCA). (Uncertainties in these and subsequent values are 95% confidence intervals.) The relatively large uncertainties in values of k_e and k_e' result from calculating small differences between two numbers of approximately equal magnitude. Because the relative uncertainty in the value of k_e' for 1122-TeCA exceeded 200%, this value was not included in subsequent analyses.

The products of 1122-TeCA dihaloelimination were *trans*-DCE and possibly *cis*-DCE as illustrated in Figure 1c. Figure 1c also shows the production of acetylene in the transformation of 1122-TeCA when FeS was present. (Samples from the PCA experiment included in Table 1 were not monitored for dichloroethylenes or acetylene.) Significant accumulation of acetylene corresponds to a decline in the concentration of TCE (Figure 1b,c), suggesting that acetylene is formed from reductive elimination of TCE, which in turn is formed from 1122-TeCA dehydrohalogenation. Transformation of TCE to acetylene was reported in ref *11*. Since *cis*-DCE was reported to be a product of TCE transformation by FeS (*11*), it is difficult to determine whether the *cis*-DCE detected as a minor reaction product in 1122-TeCA transformation by FeS came directly from 1122-TeCA dihaloelimination or from hydrogenolysis of the 1122-TeCA dehydrohalogenation product TCE. Both *cis*-DCE and *trans*-DCE, but not TCE, were detected in the transformation of 1122-TeCA by vitamin B$_{12}$ (*33*), and *cis*-DCE was the sole product detected in the transformation of 1122-TeCA by anoxic sediments (*34*), indicating that *cis*-DCE may be produced by 1122-TeCA dihaloelimination.

To determine the source of *cis*-DCE detected in the transformation of 1122-TeCA by FeS, the acetylene/*cis*-DCE product distribution ratios for the four time points in Figure 1c for which both *cis*-DCE and acetylene were detected were calculated and are shown in Table 3. While TCE transformation by FeS produced a constant acetylene/*cis*-DCE product distribution ratio of 11.8 ± 1.1 (*11*), the product distribution ratios reported in Table 3 are considerably smaller than 11.8 ± 1.1, and they appear to be increasing over time. Both observations suggest that *cis*-DCE comes directly from 1122-TeCA dihaloelimination as well as from TCE hydrogenolysis, since production of *cis*-DCE only from TCE would result in

a larger acetylene/cis-DCE product distribution ratio that was constant over time. The trans-DCE detected as a minor reaction product is more certainly the product of 1122-TeCA dihaloelimination and not TCE hydrogenolysis, since trans-DCE was not a product of TCE transformation by FeS (11).

Table 1 indicates that in addition to PCA, 1122-TeCA, and 112-TCA, two of the three remaining vicinal polychlorinated ethanes (HCA and 1112-TeCA) underwent dihaloelimination in the presence of FeS. (No products were detected in the reaction of 12-DCA with FeS after 120 days.) A hydrogenolysis product was detected for only one vicinal polychlorinated ethane (HCA) and then only as a minor product (9). Dihaloelimination has been shown to be favored over hydrogenolysis in the reductive transformation of vicinal polychlorinated ethanes by numerous other reductants (19, 33, 35−43), which may reflect the strong driving force for alkene formation (44) more than considerations associated with individual reducing species.

Hydrogenolysis products were the sole products detected for one geminal polychlorinated ethane (111-TCA) and the two halogenated methanes (CT and TBM) that were studied. (Essentially no transformation by FeS of the other geminal polychlorinated ethane, 11-DCA, was observed over 120 days.) However, mass recoveries of these hydrogenolysis products were low, particularly for 111-TCA and TBM. The best explanation for the poor mass recoveries is the formation of products that were not detected by the analytical methods employed here. For example, it was recently reported that CT was transformed to CF and CS_2 in an approximately 2:1 ratio by freshly precipitated FeS at near-neutral pH values (10). Considering the possibility that the $CF:CS_2$ product distribution ratio varies with pH, CS_2 might account for a significant percentage of the incomplete mass recovery of CT noted in Table 1. CT was also transformed to CS_2 by pyrite (45) and by aqueous bisulfide in the presence of biotite or vermiculite (13). Although CS_2 was not detected in these experiments, the concentrations at which it would be present after sample dilution or extraction would likely have been below analytical detection limits. Other products of CT transformation in related experimental systems that would not have been detected using these analytical methods and that might account for poor mass recovery include CO (13), CO_2 (13, 45), and formate (45).

Products that could account for incomplete mass recovery of 111-TCA reported in Table 1 include acetaldehyde and VC, detected in the transformation of 111-TCA by $CrSO_4$ (46). Neither acetaldehyde nor VC would have been detected using these analytical methods due to coelution with methanol using GC method B. For TBM, possible reaction products that would not be detected in these experiments include CO, detected in the transformation of TBM by rat liver microsomes containing cytochrome P-450 (47). Bromoalkanes such as TBM are also susceptible to nucleophilic substitutions in sulfide-rich waters, leading to alcohols, thiols, and dialkyl sulfides (48) that may not have been detected with these analytical methods.

Correlation Analysis. While reductive transformation of the halogenated aliphatic compounds in Table 1 by FeS led to a variety of reaction products, it is possible that these transformations share a common rate-limiting elementary reaction step. Correlation analyses were performed to explore the possibility of such rate-limiting processes and to assess the influence of different molecular properties on rate constants for FeS reductive dehalogenation. Two approaches to correlation analysis were used: a linear-free energy relationship (LFER) and a multiple linear correlation analysis. Rate constants for the transformation of TCE and PCE by FeS (11) were included in both analyses. For PCA, k_e', i.e., the rate constant for PCA dihaloelimination by FeS, was used.

For the LFER analysis, rate constants were fit to a LFER of the form (49)

$$\log k_{obs} = b_0 + b_1\left(\frac{E^{\circ}_{HAC}}{0.059 \text{ V}}\right) \quad (1)$$

where E°_{HAC} is the standard aqueous-phase one-electron reduction potential of the halogenated aliphatic compound and b_0 and b_1 are constants. Application of this LFER was based on three assumptions: (i) a common rate-limiting one-electron reduction (50)

$$R-X + e^- \rightarrow R^{\bullet} + X^- \quad (2)$$
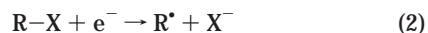
for the reductive dehalogenation of all compounds studied here; (ii) similar tendencies for adsorption of each halogenated aliphatic compound to the FeS surface; and (iii) a consistent proportionality among all compounds between the activation energy for reductive dehalogenation of the adsorbed reactant and E°_{HAC}.

An initial rate-limiting step such as reaction 2 could lead to the dihaloelimination and hydrogenolysis products reported in Table 1 (51) as well as certain products hypothesized earlier to account for the poor mass recovery of CT, 111-TCA, and TBM. For example, the transformation of CT to CF and products such as CO, CO_2, formate, and CS_2 has been explained by an initial one-electron reduction of CT followed by parallel formation of hydrogenolysis products, CS_2, and dichlorocarbene, or a dichlorocarbene adduct (13, 45, 52, 53). The dichlorocarbene or its adduct can then react with water to form CO (13, 52, 53) or formate (45), and CS_2 may subsequently undergo hydrolysis to form CO_2 (13, 45). In related experimental systems, the reductive transformation of 111-TCA has been shown to involve an initial one-electron reduction yielding a radical intermediate (54, 55). This could be followed rapidly by parallel formation of 11-DCA and a carbene intermediate (46, 56), yielding products such as acetaldehyde and VC (46). For TBM, evidence for an initial one-electron reduction to a radical intermediate has been reported (54). Parallel transformation of the resulting radical to DBM and a carbene intermediate may follow, with the carbene forming products such as CO (47).

In addition to evidence from related experimental systems, two observations from experiments with FeS are consistent with an initial rate-limiting step such as reaction 2. First, evidence was reported in ref 9 that HCA was transformed by FeS to PCE via two successive one-electron transfers. This evidence included the dependence of pseudo-first-order rate constants for HCA transformation on both HCA and FeS concentrations, indicating a bimolecular rate-limiting reaction step and detection of PCA as a reaction intermediate, which could not be produced by E2 (bimolecular) elimination and was not likely to be produced by E1cb (unimolecular elimination of the conjugate base) (9). Also, in the transformation of TCE by FeS (troilite), Sivavec et al. (6) detected hydrocarbon products hypothesized to arise from coupling of radical intermediates, consistent with a rate-limiting reaction step such as reaction 2.

Linear regression of experimentally determined log k_{obs}' values versus calculated E°_{HAC} values produced the following correlation ($R^2 = 0.48$)

$$\log k_{obs}' = -0.9 \ (\pm 1.0) + 0.14(\pm 0.14)E^{\circ}_{HAC}/0.059 \text{ V} \quad (3)$$

that is shown in Figure 2. E°_{HAC} values were calculated as described in refs 28 and 40 and are reported in Table 4. Sources for the data used in these calculations are given in the footnote to Table 4. To assess the influence of uncertainties in these values on the regression coefficients in eq 3, E°_{HAC} values for HCA, PCA, 1112-TeCA, and 111-TCA were

TABLE 4. Data Used in Correlation Analysis

compound	$E°_{HAC}$ (V vs NHE)[a]	$E°_{HAC}$ (V vs NHE)[b]	ϵ_{LUMO} (eV)[c]	$\Delta_f G°R^•{}_{(aq)}$ (kJ/mol)[d]	D_{R-X} (kJ/mol)[d]	S_{aq} (mol/L)[e]	log k_{obs}' [f]
HCA	−0.0513	−0.0985	−0.563	75.37	295.7	2.11E−4	−0.908 ± 0.026
PCA	0.00526	0.00576	−0.373	54.24	287.8	2.37E−3	−1.02 ± 0.20
1112-TeCA	−0.213	−0.0988	−0.229	65.86	305.4	6.55E−3	−1.492 ± 0.073
111-TCA	−0.318	−0.192	−0.072	84.60	316.8	1.12E−2	−1.878 ± 0.062
TCE	−0.789	NA	−0.044	223.3	357.4	6.59E−3	−2.827 ± 0.043
PCE	−0.531	NA	−0.320	204.4	334.6	1.53E−3	−3.241 ± 0.076
CT	−0.160	NA	−0.629	86.57	304.1	5.16E−3	−0.964 ± 0.054
TBM	−0.555	NA	−1.172	156.2	283.3	1.23E−2	−0.884 ± 0.050

[a] $E°_{HAC}$ values are the potentials for reaction 2 in the aqueous phase and were calculated as described in refs 28 and 40, assuming 298.15 K, 1 atm pressure, and unit activities for each reactant and product. $E°_{HAC}$ values in this column were used for the correlation in eq 3 and Figure 2. Gas-phase standard free energies for formation of R$^•$ (where R$^•$ is defined in reaction 2) were obtained or calculated from data in refs 71 (HCA, PCA, 1112-TeCA, PCE, and CT), 28 (111-TCA), 40 (TBM), or 62 (TCE). Data in these references were obtained using both experimental and theoretical methods. Gas-phase standard free energies of formation of R−X (where R−X is defined in reaction 2) were obtained from refs 72 (HCA, TCE, PCE, CT, and TBM) or 57 (PCA, 1112-TeCA, and 111-TCA). All other thermodynamic data were from ref 72. Henry's law constants were reported in the Experimental Section. Where more than one radical isomer was possible upon reduction of the halogenated aliphatic compound, the one with the smallest free energy of formation was assumed. For the one-electron reduction of PCA and 1112-TeCA, these radical isomers were $^•$CCl$_2$CHCl$_2$ and $^•$CCl$_2$CH$_2$Cl, respectively (57, 71). For TCE, cis-DCE$^•$ was assumed to form based on the calculations in ref 62. [b] $E°_{HAC}$ values in this column were calculated as described in footnote a using the gas-phase standard free energies for formation of R$^•$ from ref 57, which were obtained using the methods of statistical thermodynamics. These free energies of formation were not available (NA) for the compounds in the last four rows of this table. [c] ϵ_{LUMO} values are semiempirical values calculated using the program CAChe WorkSystem version 3.9 (Oxford Molecular Group) using PM3 parameters and MOPAC geometry optimization. [d] $\Delta_f G°R^•{}_{(aq)}$ and D_{R-X} values were calculated using the thermodynamic data and assumptions given in footnote a. [e] S_{aq} values corresponding to 25 °C are from refs 73 (HCA) and 27 (all other compounds). [f] k_{obs}' values (in h^{-1}) are from Table 1, except the values for TCE and PCE (11) and the value for PCA, which is the logarithm of k_e', i.e., the rate constant for PCA dihaloelimination reported in the text.
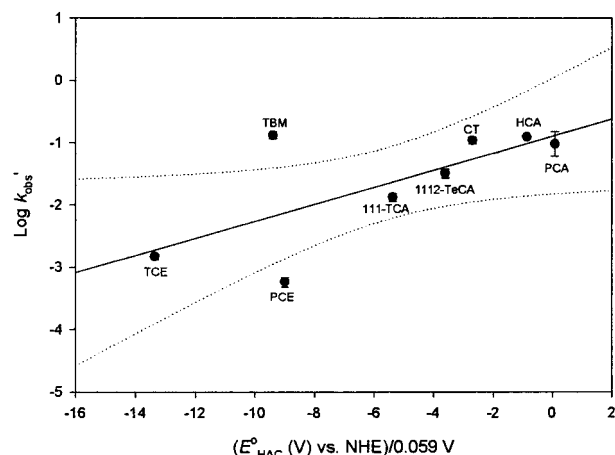

FIGURE 2. Log k_{obs}' versus $E°_{HAC}$/0.059 V. Dotted lines represent the 95% confidence interval. The linear equation is log $k_{obs}' = -0.9$ (±1.0) + 0.14(±0.14) × $E°_{HAC}$/0.059 V ($R^2 = 0.48$). Units of k_{obs}' are h^{-1}.

recalculated using a different source of thermodynamic data (57) and are reported in the third column of Table 4. (Ref 57 does not contain the thermodynamic data necessary for recalculation of $E°_{HAC}$ values for the remaining compounds.) Replotting Figure 2 using these revised $E°_{HAC}$ values for HCA, PCA, 1112-TeCA, and 111-TCA and the original $E°_{HAC}$ values for the remaining compounds yielded a linear equation [log $k_{obs}' = -1.0$ (±1.0) + 0.12 (±0.14)$E°_{HAC}$/0.059 ($R^2 = 0.43$)] that lies within the 95% confidence interval of the line illustrated in Figure 2. Although not an exhaustive uncertainty analysis, this result indicates that differences among published thermodynamic data for haloaliphatic radicals do not significantly affect the trend illustrated in Figure 2.

The slope of eq 3 is not statistically different from zero at the 95% confidence level. It is, however, significantly different from zero at the 90% confidence level, indicating a significant correlation between log k_{obs}' and $E°_{HAC}$ values at this relatively conservative confidence level. However, for one-electron reduction reactions for which the assumptions stated earlier apply, a line of the form of eq 3 will have a slope of 1 (58). The slope of 0.14 in eq 3 indicates the limitations of one or more of the previously stated assumptions.

The assumption that reaction 2 represents a common rate-limiting elementary reaction step for FeS reductive transformation would be inaccurate if FeS transformations take place by mechanism(s) other than reaction 2 or if mass transport and not chemical processes were rate-limiting. As discussed earlier, TBM may have undergone nucleophilic substitution in the presence of FeS, which may explain the deviation of this compound from the trend exhibited by the other compounds. Nucleophiles such as sulfides and polysulfides have also been shown to promote dihaloelimination reactions (39, 40, 42, 43, 59) by pathways that may involve a single two-electron reduction reaction (60), and it is possible that the sulfide functional groups in FeS promote such a reaction for one or more of the compounds studied here. The possibility that adsorption or desorption of reactants or products to or from the FeS surface were rate-limiting processes seems unlikely, since the observed rate constants are relatively small and differ from each other by 1 or more orders of magnitude (Table 1, Figure 2), while rate constants for mass transfer to or from the FeS surface are likely to be larger and more uniform in magnitude.

Significantly different tendencies for adsorption of each compound to the FeS surface could also contribute to the relatively poor correlation in Figure 2, since rate constants for transformation of adsorbed reactants are proportional to equilibrium adsorption constants under conditions where pseudo-first-order behavior with respect to the adsorbed reactant is observed (61). Different mechanisms of adsorption may also have influenced rate constants and thereby contributed to the poor correlation in Figure 2, since bonding interactions between each compound and the FeS surface could raise or lower activation energies and negate the assumption of a consistent proportionality between activation energies and $E°_{HAC}$ values. These effects may be most important for compounds with structure and properties significantly different from the others, such as TCE and PCE. Significant adsorption to nonreactive surface sites may also have influenced rate constants and contributed to the poor correlation in Figure 2.

Because the results illustrated in Figure 2 suggested that properties other than $E°_{HAC}$ influence rate constants, an empirical correlation that related rate constants to one or more molecular property was sought. The regression tech-
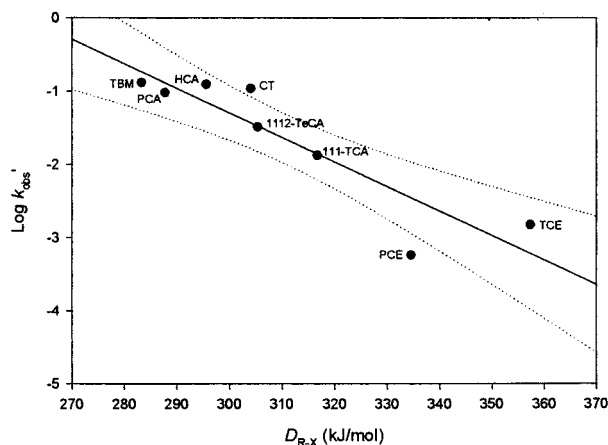
FIGURE 3. Log k_{obs}' versus D_{R-X}. Dotted lines represent the 95% confidence interval. The linear equation is log $k_{obs}' = 8.8$ (±4.9) $-$ 3.4 (±1.6) $\times$ $10^{-2} \times D_{R-X}$ ($R^2 = 0.82$). Units of k_{obs}' are h^{-1}.

niques described in ref *62* were used to determine the simple or multiple linear equation that best described the relationship between log k_{obs}' values and one or more of the following properties of the halogenated aliphatic compound: E^{o}_{HAC}, the LUMO energy (ϵ_{LUMO}), the free energy of formation of the aqueous-phase radical ($\Delta_f G^{o} R^{\bullet}_{(aq)}$, where $R^{\bullet}$ has the meaning shown in reaction 2), the gas-phase homolytic bond dissociation enthalpy (D_{R-X}), and aqueous solubility (S_{aq}). Values of these properties are reported in Table 4. The first four properties are closely related and represent one or more components of the thermodynamic driving force for one-electron reduction, while the fifth, S_{aq}, is typically related to the extent of adsorption of hydrophobic organic compounds to mineral surfaces that do not have significant organic carbon content (*63*).

The best statistically significant relationship between log k_{obs}' and one or more molecular property was a simple linear correlation between log k_{obs}' and D_{R-X} ($R^2 = 0.82$)

$$\log k_{obs}' = 8.8\ (\pm4.9) - 3.4\ (\pm1.6) \times 10^{-2} \times D_{R-X} \quad (4)$$

which is illustrated in Figure 3. S_{aq} showed the least correlation of any molecular property with log k_{obs}' values (the R^2 value was 0.01 for a simple linear correlation of the form of eq 4). This is consistent with the previously stated assumption of similar tendencies for adsorption of each halogenated aliphatic compound to the FeS surface, since significant differences among the equilibrium constants for adsorption of these compounds would likely produce a better correlation between log k_{obs}' values and S_{aq}.

As with eq 3, correlation of rate constants with D_{R-X} in eq 4 is consistent with a rate-limiting step involving radical formation such as reaction 2, since D_{R-X} is the enthalpy required for a species R–X to dissociate to $R^{\bullet}$ and $X^{\bullet}$ and reflects the ease of radical formation or radical stability. This finding is also consistent with numerous other studies in which rate constants for reductive dehalogenation have been related to both D_{R-X} and the stability of the alkyl radical generated upon bond dissociation (*14, 19, 51, 64–69*) and with the widely observed structure activity relationship of increasing rates of reductive dehalogenation in the order R–Cl < R–Br < R–I, which reflects the order of decreasing carbon–halogen bond strength (*70*).

The results discussed here indicate that FeS reductive transformations are more rapid than abiotic transformations such as hydrolysis and dehydrohalogenation under certain conditions and that molecular properties such as E^{o}_{HAC} and D_{R-X} are fairly correlated with reactivity for most of the compounds studied here. Both findings have application in

predicting the transformation of halogenated aliphatic pollutants by FeS in natural and engineered systems. However, no thermodynamic or empirical relationship accurately described the reactivity of all the halogenated aliphatic compounds that were investigated, suggesting differences among the mechanisms for reductive dehalogenation of these compounds by FeS or suggesting that parameters not addressed in the correlations also influence rate constants. This is particularly evident with PCE and TBM. It is likely that different tendencies or mechanisms of adsorption to the FeS surface play a role in determining relative reaction rates. An important goal of future studies will be to further investigate these questions.

Acknowledgments

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